ACTIVATED CARBONS FUNCTIONALIZED WITH THIOL AND SULFONIC ACID GROUPS FOR CATALYTIC WET PEROXIDE OXIDATION

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1. Introduction

Activated carbons are known catalysts for hydrogen peroxide decomposition through a pathway involving the formation of hydroxyl radicals [1]. Thus, it seems logical to take advantage of the strong oxidizing properties of these radicals for the degradation of organic pollutants adsorbed and concentrated on the surface of activated carbons. In a recent work, we established the unprecedented performance of acidic activated carbons functionalized with sulphuric acid in the catalytic wet peroxide oxidation of Chromotrope 2R, an anionic azo dye [2]. In the present work, we explore the influence of the amounts and types of surface groups with sulphur on the catalytic efficiency of the activated carbons.

2. Experimental

The activated carbon Norit ROX 0.8 (AC) was submitted to liquid phase chemical modification treatments with sulphuric acid (as described in Table 1) producing materials with different chemical surfaces (labelled as ACSA). The textural properties of the carbon materials were obtained by the N_2 adsorption-desorption isotherms. The surface chemistry was characterized by temperature programmed desorption (TPD), determination of PZC and titration of acidic and basic active sites. The oxidation experiments were performed with 100 mg/L Chromotrope 2R (C2R) aqueous solutions at 50ºC, pH = 3, 0.5 g/L of catalyst and 34.6 mM of hydrogen peroxide (corresponding to nearly 5 times the stoichiometric amount needed to completely mineralize C2R).

3. Results and discussion

From the N_2 adsorption-desorption isotherms (not shown), it was observed that the treatments with sulphuric acid do not affect in a great extent the textural properties of the original material. On the other hand, significant differences were observed regarding the acid/base character of the tested materials, as shown in Table 1.

Table 1. Activated carbons studied in this work: chemical characterization.

Catalyst	Treatment with sulphuric acid		PZC	Acidity	Basicity
	Temperature (K)	Concentration (M)	(± 0.1)	(± 10 μmol.g^{-1})	(± 10 μmol.g^{-1})
AC	-	-	7.6	360	530
ACSA1	353	5	5.8	800	300
ACSA2	353	10	4.1	830	210
ACSA3	353	18	2.4	920	200
ACSA4	423	5	5.5	760	250
ACSA5	423	10	3.8	880	200
ACSA6	423	18	2.0	1000	190

While the original AC possesses an evident basic character, the treatments with sulphuric acid produced materials with a markedly acidic character, with a magnitude dependent on the strength of the acid solution used in the treatment. The increase in the concentration of acidic surface groups is mainly due to the introduction of thiol and sulfonic acid groups, as concluded from analysis of the TPD spectra (not shown). The PZC values of all materials are well in accordance with their acidic character – lower the PZC, higher the acidic character.

The initial removal rates of C2R obtained with the tested activated carbon materials, either in adsorption and reaction experiments, are given in Figure 1.

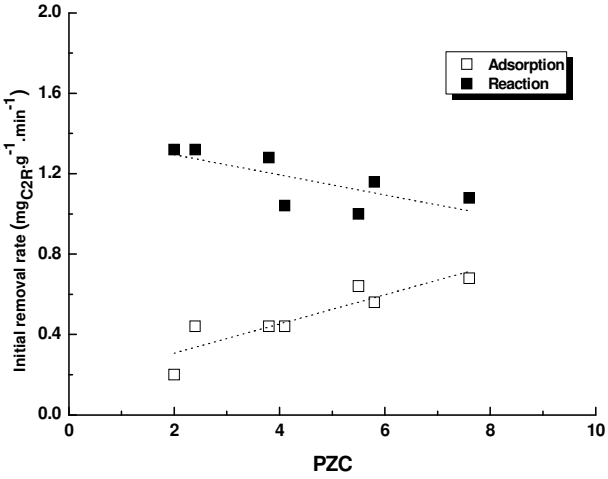

Figure 1. Initial removal rates of C2R in adsorption and reaction experiments at 50ºC as function of PZC for each carbon sample.

In general, dye removal by adsorption is increased when using activated carbons with lower acidic character, due to the enhanced electrostatic attraction between the acid dye and the surface [3]. On the other hand, the increase in global removal rate by reaction contribution with increasing acidic character can be ascribed to the presence of higher concentrations of thiol and sulfonic acid groups, through different reaction pathways which contribute to chemical pollutant removal in addition to physical mechanisms. Sulfonic acid groups have a strong hydrophilic character, increasing the wetting of the ACSA materials in aqueous solution, thus increasing the corresponding adsorption of dissolved hydrogen peroxide molecules (which is also favoured by the reduced adsorption of C2R). This is crucial to generate hydroxyl radicals at the catalyst surface in the vicinity of C2R to promote further reaction. The presence of thiol groups on the surface of ACSA is also fundamental due to the role of these groups in the efficient homolysis of the adsorbed hydrogen peroxide molecules to generate hydroxyl radicals.

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5. References

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